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**Field sampling of soil pore water to evaluate the mobile fraction of trace elements in the
Iglesiente area (SW Sardinia, Italy)**

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Abstract

Field soil pore water monitoring was applied in a highly heavy-metal contaminated area in SW Sardinia, Italy, as a direct, realistic measure of heavy metal mobility. The main chemistry of pore waters well reflects the local characteristics of soils, ranging from Ca-SO₄ to (Ca)Mg-HCO₃ to Ca(Na)-SO₄(Cl), with a wide range of conductivity. The mobility of Zn and Pb is apparently controlled by equilibrium with minerals such as hydrozincite or smithsonite, and cerussite, respectively. These results allow a correct estimate of the actual environmental risk associated with the presence of heavy metals in soils, and may serve as a supporting tool for phytoremediation planning.

Key words: soil pore water; heavy metal mobility; Iglesiasiente (Sardinia)

1. Introduction

The presence of potentially toxic chemical elements (PTEs) in soils, either naturally occurring or from anthropogenic activities (such as, amongst others, mining activity), represents a serious environmental threat, involving the entire system of relationships between hydrosphere, geosphere and biosphere (Nkongolo et al., 2013; Li et al., 2014). In the past century, mining was the driving sector of the economy in south-western Sardinia (Italy). Mining industry began to decline around the end of the century, leading to the closure of most mines over the 1970–1990 period. There are now in the region about 170 abandoned mines, and 200 million tons of mining-related wastes,

29 covering a surface of 19 km² (RAS, 2003; Ardau et al., 2013). Due to the ineffective or totally
30 absent management of mining-related wastes in the last decades, in several Sardinian areas the PTE
31 contamination extended to the surrounding environment, affecting air, water and soils (e.g. Aru et
32 al., 1995; Vacca & Vacca, 2001; Cidu et al., 2001; Concas et al., 2006; Cidu et al., 2011; Fanfani &
33 Ardau, 2011; Vacca et al., 2012; Cidu et al., 2012; Ardau et al., 2013).

34 In abandoned mining areas, removal, treatment or confinement of mining-related wastes may
35 be not viable for several practical reasons, including the extremely high costs (Lomelin, 2002;
36 González et al., 2006; Ardau et al., 2013). A ‘soft’ alternative is represented by phytoremediation
37 (Barbafieri et al., 2011), that includes two different options: phytostabilization and phytoextraction
38 (Chaney et al., 1997). Phytoextraction may represent a valuable, cost-effective alternative to
39 traditional disruptive technologies (Cao et al., 2007), but it is often of limited application. A more
40 widely applicable technique is phytostabilization, because the quick establishment of a dense
41 vegetation cover is crucial to limit wind and water erosion. Moreover, plant roots may immobilize
42 metals by adsorption or accumulation, and provide a rhizosphere wherein metals precipitate and
43 stabilize (Mendez & Maier 2008; Cao et al., 2009; Nicoară et al., 2014).

44 One of the prerequisites for phytoremediation planning and management is to identify mobility and
45 phytoavailable fraction of (toxic) chemical components in soil/wastes. From many studies
46 (Impelliteri et al., 2003; Tye et al., 2003; Cui et al., 2014), it is well established that total soil/waste
47 metal content alone is not an adequate measure of the potential mobility of a (toxic) element and,
48 consequently, of its possible uptake by plants (Vig et al., 2003; Di Bonito et al., 2008; Barbafieri et
49 al., 2011). Therefore, chemical methods to determine trace metal phytoavailability in soils are
50 usually based on the measurement of the extractable or labile fractions of those elements (De Siervi
51 et al., 2004). However, there is no agreement on how to evaluate at best the risk arising from the
52 fraction of pollutants that are most mobile in soils (Sneddon et al., 2006; Vázquez et al., 2008;
53 Moreno-Jiménez et al., 2011). Among the possible methods of identification, the direct
54 measurement of the composition of soil pore waters is being increasingly applied, due to many

55 advantages in term of simplicity and costs (Meers et al., 2007; Di Bonito et al., 2008; Beesley et al.,
56 2010; Moreno-Jiménez et al., 2011; Shaheen et al., 2014).

57 In the present study, the composition (major element chemistry and selected heavy metal
58 contents) of soil pore water was determined in a highly heavy-metal contaminated area included in
59 the Iglesias mining district (south-western Sardinia, Italy), one of the largest of the island, and of
60 importance at the European scale. To the best of authors' knowledge, this is the first time that this
61 technique is applied in the district. The study area is located in a geographic region with a typically
62 Mediterranean climate, with very dry summers, and is characterized by natural geochemical
63 anomalies (particularly Pb, Zn, Ba), enhanced by centuries of mining activity (Bechstädt et al.,
64 1994; Boni et al., 1999). The monitoring of temporal, local and spatial variations in pore water
65 quantity and quality was carried on from a series of undisturbed soil/mine waste profiles. The study
66 is a significant part of a more extended project (Concas, 2014). In a companion paper (Concas et al.,
67 submitted), the metal uptake by an endemic Mediterranean species (*Pistacia lentiscus* L.) was
68 assessed. Although not part of this specific paper, some recall to that supplementary information
69 will be made for a more robust data discussion.

70

71 **2. Materials and methods**

72 *2.1 Study site*

73 The Iglesias mining district (Sardinia, Italy) was for centuries up to the 1990s the seat of intense
74 mining activity. The ore bodies are hosted in Cambrian dolomites and limestones, and produced
75 some hundred million tons of Zn–Pb–Ag and Ba ores (Boni et al., 1999, and references therein).
76 The cessation of mining activity left large quantities of mine wastes in dumps and flotation tailings
77 basins, estimated at about 45 million m³ for the whole area (Cao et al., 2009).
78 Concas (2014) describes a total of 9 soil profiles in 5 sites in the basin of the San Giorgio river,
79 having an extension of about 2,563 ha (Fig.1). Four main representative sites were selected for this
80 study. The first site (*Campo Pisano*) is located near the town of Iglesias, the main urban centre of

81 the area. Campo Pisano is one of the hazard centres of the district because of the presence of waste
82 impoundments where, during mining activity in the 1900s, flotation wastes from several mines of
83 the district were collected, in particular from Monteponi mine (Cidu et al., 2001, RAS, 2003). The
84 flotation wastes (about 8 million m³) contain Pb and Zn as the most abundant heavy metals. Due to
85 the high heavy metal concentrations, low organic carbon, and low cation exchange capacity, the
86 flotation wastes area appears bare and unvegetated (Cao et al., 2009). Specifically, samples for this
87 study (sampling points P1 and P3 in Fig. 1) were collected from two different experimental plots
88 used for a previous revegetation test with endemic species (*Pistacia lentiscus* L.; Bacchetta et al.,
89 2012). P1 samples are from a plot representing the untreated waste material, while P3 samples are
90 from a plot where some compost was added. Since planting in 2008, *P. lentiscus* survived only in
91 the P3 plot (Fig. 2).

92 The second and third sampling areas are two natural sites, not visibly affected by morphological
93 alterations due to mineral extraction, located in the natural substrate of Cambrian limestones and
94 dolostones, that host the metalliferous bodies (sampling points P5 - *Serra Merareddu*, and P6 -
95 *Pozzo Santa Barbara* - Fig. 1). These sites, characterised by natural geochemical anomalies
96 (particularly in Zn and Pb), though not intended to statistically represent the whole district, can give
97 an idea of pre-mining conditions. In both sites *P. lentiscus* grows spontaneously. The fourth site is a
98 lagoon deposit at *Sa Masa*, near the Funtanamare beach (sampling point P9 in Fig.1), final collector
99 of waters and pollutants from the entire watershed of the San Giorgio river (including mining
100 seepages, and sewage waters from the Iglesias town). Therefore, the high contamination at Sa Masa
101 (see below) is not just site specific, but induced by transportation of solid and liquid matrixes from
102 other localities within the San Giorgio basin. Even at Sa Masa, *P. lentiscus* grows spontaneously.

103 As previously noted, the climate of the area is typically Mediterranean, characterised by very dry
104 summers. The maximum annual average temperature is 25°C, and the minimum 5°C. Average
105 annual precipitation is ca. 800 mm (<http://my.meteonetwork.it/station/srd025/statistiche>).

106

107 2.2 Soil characterization

108 At each study site, a soil profile was opened and described, making a distinction in pedogenetic
109 horizons according to standard procedures of soil description (Schoeneberger et al., 2002); samples
110 of each horizon were collected for subsequent laboratory analyses. Even though Campo Pisano is
111 not classifiable as natural soil, for descriptive purposes the terms ‘soil’ and ‘soil horizon’ are also
112 used for that site, where the substrate is in fact mainly composed of mine tailings. This study
113 considers data from shallow, unsaturated horizons, according to the lysimeter or rhizometer depths
114 used for field soil pore-water extraction (see below). The complete set of soil data is available in
115 Concas (2014).

116 Bulk soil samples were air-dried and sieved (<2 mm, fine earth). Routine physical and chemical
117 analyses were carried out according to the procedures published by the Italian Ministry of
118 Agriculture (MiPAF, 1998, 2000). Sand (2.00–0.05 mm), silt (0.050–0.002 mm) and clay (<0.002
119 mm) fractions were separated after the removal of organic matter by H₂O₂ treatment and dispersion
120 aided by Na-hexametaphosphate by the sieve and pipette methods. The soil pH was measured in a
121 1:2.5 soil/water suspension. The organic carbon (OC) was estimated by wet digestion with a
122 modified Walkley–Black procedure. Soils were classified according to IUSS Working Group WRB
123 (2014). Mineralogical analyses were performed on the <2 mm fraction by powder X-ray diffraction
124 (PXRD), on an automated Panalytical X'pert Pro diffractometer with Ni-filter Cu-K_{α1} radiation ($\lambda =$
125 1.54060 Å), operating at 40 kV and 40 mA, using the X'Celerator detector (see 4.1 paragraph). The
126 main soil chemical components (major element oxides for ordinary rocks) were also determined on
127 the <2 mm fraction by a Philips PW1480 wavelength-dispersive X-ray fluorescence (WDXRF). For
128 the A horizon at the P9 location, it was not possible to obtain a suitable pellet for XRF analysis,
129 because of its loose incoherent texture. Information on its ‘major oxide’ content is not critical for
130 the purposes of this paper, and we made no further efforts to obtain these data. Raw intensities were
131 corrected for matrix effects by the method of Franzini & Leoni (1972), making reference to
132 certified rock standards. The method is calibrated for ordinary rocks, with comparatively low heavy

133 metal contents. The correction routine does not adequately account for the unusually high contents
134 of Pb and Zn typical of most of our samples. Therefore, XRF data should be taken as semi-
135 quantitative. Loss of ignition (LOI) was determined by leaving an aliquot of the sample at 900°C
136 for 8 hrs, and expressed as percent weight difference before and after the treatment. Contributions
137 to LOI include carbonate decomposition, dehydration of clay minerals and/or Fe-Al oxyhydroxides,
138 and burning of organic matter. The total heavy metal contents of soil samples were determined on
139 the <2 mm fraction after digestion in microwave system (Milestone Ethos 1 oven) with a
140 HNO₃/HF/HClO₄ (5:2:1 v/v) mixture, as proposed by Brunori et al. (2005), analysing the obtained
141 solutions by an inductively coupled plasma optical emission spectrometer (ICP-OES Analyzer,
142 ARL Fisons 3520B). Soil samples were randomly digested and analysed in replicate to test the
143 precision of the method. In this case the average datum of the two aliquots was considered. The
144 accuracy was tested against the certified standard NIST 2710. Overall, heavy metal analyses in soils
145 are within $\pm 10\%$ for both accuracy and precision.

146

147 *2.3 Soil pore water sampling and analyses*

148 At each study site soil pore water samples were collected from unsaturated profiles, in the rooting
149 zone. In order to reduce as much as possible soil disturbance during sample collection SPS 200 soil
150 water samplers (SDEC, France) were used (Lekakis et al., 2015). The samplers, namely 'vacuum
151 lysimeters', are characterised by a porous ceramic cup glued on the bottom of an empty PVC tube
152 (31 mm in diameter), and are designed to replicate the suction function of plant roots.

153 The samplers were placed in all sampling points at 10-15 cm depth into the upper soil horizon, and,
154 when possible, at 30-40 cm depth into the underlying horizon. At P1 and P3, only short lysimeters
155 were used, because of the shallow depth of soils. Before starting the sampling, the lysimeters were
156 left for 1 month in the field to equilibrate. One day before sampling, a vacuum of -75 kPa was
157 created inside the tube with a vacuum pump (SPS400, SDEC, France), through a connecting tube
158 hosted in a pierced rubber bung, in order to draw the pore water from the soil to the porous ceramic

159 cup and into the tube. To sample the pore water, the vacuum pump was used to collect the soil
160 solution contained in the tube, which was then poured into a sampling flask. Because of the climate
161 of the area, with very dry summers, four surveys were carried out between the rainiest period,
162 corresponding to the winter, and the starting of the dry season (from December 2012 to April 2013).
163 In fact, fall 2012 was unusually dry, and at the time of the first sampling (December 2012) it was
164 possible to obtain enough liquid for analysis only at Campo Pisano and Sa Masa. In the following
165 months (January – February 2013), there was enough rain infiltration to allow collection of
166 sufficient pore water from most lysimeters. In April 2013, with the beginning of the dry season,
167 only at Sa Masa, where the water table was always shallow, it was possible to collect soil pore
168 water. At this site in April 2013 three additional samples were collected using another type of
169 tension sampler, namely the 'rhizon sampler' or 'rhizometer' (Eijkelkamp Agrisearch Equipment,
170 The Netherlands) (Tye et al., 2003; Di Bonito et al., 2008). Using this device, pore water solution is
171 extracted by inserting it into the soil, and connecting a syringe for applying the vacuum and then a
172 suction. Sampling points were two at Campo Pisano (sampling points 1 and 2, respectively at P1
173 and P3), three at the Serra Merareddu (P5) site (sampling points 6a, 6b and 6c), where letters a, b
174 ...indicate that lysimeters were positioned all around the same *P. lentiscus* individual; three at the
175 Pozzo Santa Barbara (P6) site (sampling points 7a, 7b and 7c), and eight at the Sa Masa (P9) site,
176 respectively five sampled by lysimeters (sampling points 4a, 4b, 4c and 5a, 5b), two by rhizometer
177 (sampling points 19 and 22), and one sampled by both (sampling point 25).

178 Pore waters collected with lysimeters were filtered to 0.45 μm ; for solutions extracted by rhizon
179 samplers this filtering is not necessary, because their porosity is less than 0.45 μm . Labile
180 parameters (temperature, pH, conductivity) were measured in the field. Because of the scarcity of
181 collected liquid, Eh was not routinely determined; in the few samples where it was measured, the
182 values indicate oxidising conditions (equilibrium with the atmosphere), as expected for unsaturated
183 horizons. The solutions were stabilised to 1% v/v with HNO_3 for the subsequent analyses of major
184 and trace elements, including heavy metals. Whenever enough solution was available, total

alkalinity was determined independently by HCl titration on another aliquot. The major elements were measured by Ion Chromatography, and the trace elements (Zn, Pb, Cd, Mn, Fe, Cu) by ICP-OES (Perkin Elmer Optima 2100 DV). Because of solution scarcity, anions were determined on the same acidified aliquot used for cations; obviously, this made impossible the measure of nitrate in solution. In Sardinia, high (>50 mg/L) nitrate content in groundwaters is mostly linked to agriculture (RAS, 2010), which is not the land use of any of the studied sites. Moreover, ionic charge balances (see below) do not suggest anion deficit in any of the analyzed pore waters. In some cases (data marked with * in Tables 3a and 3b), when the solution from a single sampling was not sufficient for the analyses, pore waters from two close sampling points were combined. The dissolved organic carbon (DOC) was determined by TOC/TN analyser (Analytical Sciences Thermalox program), a specific instrument for total organic carbon and nitrogen contents in water solutions. The instrument actually determines the total carbon (TC); whereas the dissolved inorganic (carbonate) carbon (DIC) is removed by acid addition, and the remaining DOC is measured by a second pass in the TOC analyser. The inorganic carbon is calculated as the difference between TOC and DIC. When it was not possible to collect enough pore water for an independent determination of alkalinity, the value of DIC was used to calculate alkalinity as HCO_3^- . Quality control of pore water chemical analyses is intrinsically difficult. To the best of authors' knowledge, there are no specific certified international standards, and replicate analyses were seldom possible. Preliminary release tests with deionised water on new lysimeters and rhizometers indicated negligible (below detection limits for ICP-OES) amounts of released elements, except for Ba. For this element, high values were recorded in lysimeter blanks, therefore data for Ba were not included in this study. Field blanks were obtained by introducing deionised water in the same devices used for pore water samples, and treating the collected volumes as independent samples. The accuracy of ICP-OES analyses was checked with calibration standard solutions. A further check of quality of analysis for major elements are ionic balances. From data in Table 3b, it is

possible to calculate ionic balances: most are within $\pm 10\%$, and only two are within $\pm 15\%$. Overall, it is estimated that most of analyses are within $\pm 20\%$ error for both accuracy and precision. The collected data were elaborated with two different speciation programs, PHREEQC 3.0.2 (Parkhurst et al., 1980; Parkhurst, 1995) and WHAM 7.0.2 (Tipping, 1994); specifically, the second accounts for complexation of metals by organic matter.

3. Results

3.1 Soil characterization

Field observations, summarized in Table 1, showed that (i) the soil derived from untreated waste material (P1) is shallow, and characterized by a very thin cemented and hardened surface horizon overlying two mineral horizons slightly enriched in organic carbon (OC); (ii) the soil derived from the waste material treated with compost (P3) is shallow, and characterized by a ploughed epipedon enriched in OC; (iii) soils derived from dolomitic limestones (P5 and P6) are shallow or moderately deep, with A horizon at surface and a well expressed Bw horizon, and lithic contact toward the underlying bedrock; (iv) the soil derived from Holocene lagoon deposits at Sa Masa (P9) is deep, and characterized by a sequence of different sedimentary cycles (marked by differences in texture). The differences in texture among the soils (Table 1) reflect their origin from different parent materials, and confirm the field assessment. Reaction is generally neutral to slightly alkaline, with the exception of the strongly acid 2^AC horizon of P1 and P3, and the moderately alkaline 5C4 and 6C5 horizons of P9. OC contents are highest in the surface horizons and decrease regularly with depth.

In the World Reference Base (WRB), the studied soils classify as follows: Spolic Technosol (P1 and P3), Endoleptic Luvisol (Abruptic, Humic, Clayic, Rhodic) (P5), Epileptic Luvisol (Abruptic, Humic, Chromic) (P6), and Haplic Fluvisol (Calcaric, Ruptic) (P9).

235 The main physicochemical characteristics of the studied soils are reported in Table 1, while
236 mineralogical composition is described hereafter. At Campo Pisano (P1 and P3), tailings
237 mineralogy is dominated by the presence of quartz, gypsum and carbonates (mainly dolomite,
238 secondarily calcite and traces of ankerite), with minor muscovite and microcline, and residual
239 pyrite. Hydrozincite, cerussite, as well as traces of sphalerite and galena, were also detected in some
240 horizons.

241 Samples from Serra Merareddu (P5) and Pozzo Santa Barbara (P6) contain a clay component
242 (kaolinite and montmorillonite), as expected in *sensu stricto* soils. The main mineral at both sites is
243 however quartz (possibly of aeolic deposition: Concas, 2014). Dolomite is the predominant
244 carbonate; barite occurs in all profiles. At Sa Masa (P9), carbonates (calcite, dolomite, and
245 subordinate ankerite) and quartz represent the main minerals. Minor minerals include
246 hemimorphite, barite, and cerussite. As observed above, at Sa Masa some mineral component could
247 result from transport from other localities.

248 The main chemical composition (Table 2a) is substantially in agreement with the mineralogy of
249 soils. High LOI and CaO values in samples from Campo Pisano and Sa Masa are indicative of the
250 presence of a major carbonatic fraction, while in P5 and P6 profiles the prevalence of the quartz and
251 phyllosilicate fraction is well pinpointed by high values of SiO₂ and Al₂O₃. Iron (as Fe₂O₃) is
252 significant, as expected, in the tailing samples from Campo Pisano (P1 and P3), where, other than in
253 residual pyrite or ankerite, it could be also present as poorly crystalline Fe-oxide-hydroxides from
254 sulphides oxidation, such as ferrihydrite (Blowes et al., 2003; Marescotti et al., 2012; Ardaù et al.,
255 2014), not easily identifiable by PXRD analyses in complex matrixes; the site with the lowest Fe is
256 Sa Masa.

257 Among heavy metals (Table 2b), Zn concentration is around thousand mg kg⁻¹ at Pozzo S. Barbara
258 (P6), from thousand to ten thousand mg kg⁻¹ at Campo Pisano (P1 and P3) and Serra Merareddu
259 (P5), from thousand to hundred thousand mg kg⁻¹ at Sa Masa (P9). Lead concentrations vary from
260 thousand mg kg⁻¹ at Campo Pisano and Pozzo S. Barbara, and from thousand to ten thousand at

261 Serra Merareddu and Sa Masa. Cadmium and Cu are present in amounts around tens mg kg⁻¹ in all
262 sites, except at Sa Masa where concentrations can reach hundreds mg kg⁻¹.

263 As it can be observed from chemical results, the natural soils at P5 and P6 sites show heavy metal
264 contents of the same order of magnitude as the mining flotation waste at Campo Pisano. Some
265 values are in fact higher than median values of stream sediments in the district (Boni et al., 1999),
266 which can be taken as an indication of the local post-mining geochemical baseline. Concas (2014)
267 reports that at these sites the rock substrates (R layer) show appreciably lower metal contents,
268 suggesting that either the sites are in some way contaminated by anthropic activities (e.g., by wind
269 transport from nearby mine sites), and/or pedogenetic processes led to a (passive) enrichment in
270 some heavy metals. This issue is beyond the purpose of this paper, and it will not be further
271 discussed.

272

273 *3.2 Pore water chemistry*

274 The overall major element chemistry of pore water samples, distinguished for location, is depicted
275 in the Piper diagram of Fig. 3. Tables 3a and 3b and 4a and 4b report the main physical and
276 chemical parameters (including major and selected trace components) of the studied pore waters,
277 divided for location and sampling periods.

278 Fig. 3 points out a clear difference among pore water major chemistry of Campo Pisano samples
279 (P1 and P3) from the natural substrate of Cambrian limestones and dolostones (P5 and P6), and
280 from Sa Masa (P9). In terms of descriptive hydrochemical facies (e.g., Back, 1966), the Campo
281 Pisano waters belong to a Ca-SO₄ type, those of P5 and P6 to a Mg-HCO₃ type (with a subordinate
282 Cl component for some samples), and those at Sa Masa again to a Ca-SO₄ type, but with a
283 significant Na-Cl component, presumably reflecting a marine input, either from seawater ingressión
284 or from sea spray deposition (see further discussion).

285 Conductivity of pore waters is highly variable, ranging from ~570-900 µS cm⁻¹ in samples from the
286 natural substrate, ~1200-2000 µS cm⁻¹ at Campo Pisano, up to ~2400-3700 µS cm⁻¹ at Sa Masa,

287 indicating that the overall amount of soluble minerals, influencing pore water components, is rather
288 different in the three sites. Moreover, at Sa Masa a direct influence of the sea water component (see
289 below) in the high conductivity is likely. The pH of pore waters shows a moderate range of
290 variation (from circumneutral to alkaline) for different sites and/or different sampling times.

291 With respect to trace elements, zinc presents the highest concentration at Sa Masa, in the order of
292 thousand $\mu\text{g L}^{-1}$, in particular at the deepest levels (up to $5700 \mu\text{g L}^{-1}$, with the only exception of the
293 December 2012 sampling, when Zn does not exceed hundreds $\mu\text{g L}^{-1}$). At Campo Pisano, Zn
294 concentrations are around hundreds $\mu\text{g L}^{-1}$ (no substantial differences are observed between plots
295 P1 and P3). As observed at Sa Masa, concentrations are one order of magnitude lower during
296 December 2012 sampling. The lowest Zn concentration (averagely of tens $\mu\text{g L}^{-1}$) is recorded at P5
297 and P6, where December 2012 sampling was not possible for the absence of sufficient water (see §
298 2.3).

299 Lead concentrations are in the order of tens $\mu\text{g L}^{-1}$ in all sampling sites, in agreement with the
300 known low mobility of this metal at pH values >7 . The highest concentrations are registered in
301 January 2013 at Serra Merareddu, which is also the site with the highest total Pb values in the soil.

302 Manganese concentrations may show a certain variability in samples of the same site (e.g. 4a, 4b,
303 4c); in general, this metal is more abundant at Sa Masa (up to hundreds $\mu\text{g L}^{-1}$). At Campo Pisano
304 Mn does not exceed tens of $\mu\text{g L}^{-1}$, while it is close or below the limit of detection in the natural
305 soils (P5 and P6).

306 Iron does not show high mobility, in spite, for example, of significant bulk soil concentrations at
307 Campo Pisano. In fact, as expected at pH values measured in the pore waters, Fe results strongly
308 bound to the solid fraction of the soil (e.g. Ardaù et al., 2009), and therefore, often below the
309 detection limit in the pore water. When detectable, the saturation index (SI^1) modelling results (not
310 shown) indicate high oversaturation with respect to the most abundant Fe-oxide-hydroxide in

¹ Saturation index (SI) = $\log (\text{IAP}/\text{K}_{\text{sp}})$, where IAP (ion activity product) is the product of the chemical activities of the dissolved ions of the mineral, and K_{sp} is the solubility product. SI shows whether a particular mineral is in equilibrium with solution (SI null), or will tend to dissolve (SI negative), or precipitate (SI positive)

311 mineralised areas, such as goethite or ferrihydrite. Iron is also the metal showing the highest local
312 variability as a function of sampling period (see for example P1), indicating a strict seasonality
313 relationship.

314 As expected from their comparatively low bulk soil concentrations, Cd and Cu are definitely
315 subordinate in pore waters of all sites.

316 The OC content varies from undetectable ($<0.04 \text{ mg L}^{-1}$) up to 12.6 mg L^{-1} at Campo Pisano. OC
317 contents in pore waters are not clearly related to bulk OC in soils. Presumably, this finding reflects
318 different degrees of solubility of organic matter in the different sites.

319 Speciation equilibria, as calculated by PHREEQC and WHAM, are summarised in Table 5.

320 Calcium and Mg are mostly present as free ions (average 70-80% in all samples). In the natural
321 substrate (P5 and P6), Ca and Mg also show a subordinate association with carbonate species (CO_3
322 and HCO_3), while in sulphate-rich pore waters (Campo Pisano and Sa Masa) a subordinate
323 association with SO_4 is shown. As a general rule, all samples reach equilibrium or oversaturation
324 conditions with respect to calcite and dolomite (Fig 4a,b). Gypsum equilibrium is close to be
325 attained for samples from Sa Masa and Campo Pisano, while samples from natural substrate result
326 undersaturated with respect to it (Fig 4c).

327 Trace metals show a variety of species, the abundance of which is related either to the main water
328 composition, or to the specific behaviour of the element. PbCO_3 , for example, is generally the most
329 abundant Pb species both in carbonate and in sulphate waters; a subordinate species for this metal is
330 PbOH^+ . All samples are close or in equilibrium with cerussite (Fig. 4d), and undersaturated with
331 respect to anglesite (Fig. 4e).

332 Zinc mainly occurs as Zn^{2+} and subordinately as ZnSO_4 . Several samples are close to equilibrium
333 with hydrozincite, but a few are strongly undersaturated (Fig. 4f). Hydrozincite was in fact
334 identified by PXRD in some samples. Smithsonite (Fig. 4g) is consistently undersaturated, but a
335 number of samples at Sa Masa are close to equilibrium with it. This mineral was never positively
336 recognized in the studied samples, but its widespread occurrence in the district is well documented.

Specifically, smithsonite has been recognized both in the 'red muds' tailings at Monteponi and at Campo Pisano, often in association with hydrozincite and hemimorphite (the so-called 'calamine' ores of the Iglesias mining district were typically composed of Zn (hydroxy-) carbonates and silicates; Boni et al., 2003). Runoff from these wastes may well be transported to Sa Masa by the San Giorgio river.

Manganese occurs as free ion, or as ion pair with SO_4 and CO_3 . Several pore waters are close to or above saturation with rhodocrosite (Fig. 4h). This phase was not recognized in the studied samples; alternatively, the phase(s) controlling Mn in pore waters could be solid solution(s) with calcite and/or dolomite.

Cadmium mainly occurs as CdCl^+ and Cd^{2+} , and copper as CuCO_3 and CuOH^+ ; moreover, this metal is the only one for which the fraction bound to colloidal fulvic acids (as calculated by the WHAM program) is important (up to 99%). It is difficult to identify the possible phases controlling the mobility of Cd and Cu, since these elements are presumably present as minor substituting ions both in primary and secondary phases, therefore they do not appear in mineral theoretical formulas as identified by the speciation program.

352

353 **4. Discussion**

This study supports field monitoring of soil pore water chemistry as a useful method to evaluate the environmental risk associated to the mobility of (toxic) elements. With respect to indirect methods (selective and/or sequential extractions), it is comparatively rapid, because it does not require the extraction step(s); moreover, it directly records field conditions, that may imply different metal mobilities in the same soil (as shown in this study by differences in sampling events at the same sites). An additional important aspect is that pore water chemistry well reflects the 'history' of the associated soil/waste, being not merely the expression of the local mineral and chemical composition of soil/waste, but also of its 'use', geographic and climatic context. In fact, from pore water data treatment emerged some distinctive marks to distinguish among the natural mineralised

363 soils, the mine waste 'soils', and the soil from a 'collecting' area, selected for this study. If
364 mineralogical composition is generally the main factor influencing pore water chemistry, an
365 interesting exception, linked to the geographic context, is represented by Sa Masa swamp soil. At
366 Sa Masa, the influence of the near sea in the main chemistry of pore water overlaps that of soil
367 mineralogy, while trace elements show the mark of the accumulated material from different mined
368 areas present in the S. Giorgio basin, in particular for the high presence of Zn, which turned out to
369 be the most mobile metal. Sa Masa site represents, therefore, a clear example on how the mere use
370 of the total metal content in order to evaluate potential environmental risk of a contaminated soil
371 may offer indication far from those obtained by the use of pore water.

372 At Campo Pisano (P1 and P3), we are not in presence of a *sensu stricto* soil, but the substrate is
373 composed of mining wastes. This nature of the 'soil' is well pointed out by a main chemistry
374 dominated by Ca-SO₄, reflecting the abundant presence of gypsum, secondary product of sulphide
375 oxidation (as a source of sulphate), and carbonates (as a source of calcium). The heavy metal
376 contents reflect their mobility at the pore water pH values (for example with a prevalence of Zn
377 with respect to Pb) and of their solid-speciation (see below).

378 In the natural substrate of Cambrian limestones and dolostones (P5 and P6), pore water chemistry
379 well marks the difference with respect to mined areas, mainly for a limited conductivity, indication
380 of a reduced reactivity of mineral phases. However, the field pore water is perfectly able to identify
381 the presence of a geochemically anomalous area. The main chemistry is dominated by the
382 carbonatic nature of the substrate, while sulphates, indicative of possible sulphide presence and of
383 their subsequent oxidation, are limited. The lower contents in Zn in pore waters from this site with
384 respect to Campo Pisano well reflect a limited reactivity of minerals in an undisturbed soil with
385 respect to a mining waste dump. Lead is an exception since, regardless of its total concentration in
386 soils, its pore water concentration is similar and comparatively low for all sites, probably because of
387 saturation with respect to cerussite.

388 In sites where lysimeters were positioned in more than one point (see paragraph 2.3), pore waters
389 variations in different sampling points are not significant, with the only exception of Mn. Variations
390 related to the sampling period were more significant. Salinity at Sa Masa was higher in December
391 2012, and lower in February and April 2013. As shown in Fig. 5, this trend of salinity variation is
392 matched by seasonal variations of both Na and Cl (and of SO₄ – not shown), suggesting that sea
393 water contributions prevail at this site. For lagoon deposits like Sa Masa, contributions of seawater
394 may be linked either to marine ingressions, and/or to dissolution and infiltration of sea spray
395 deposited on the soil surface. Both phenomena are usually more pronounced during dry periods.
396 The input of sea salts from marine aerosol in groundwater (and surface water) close to the coast is a
397 well known phenomenon due to the dissolution by the rain of the particulate deposited on the
398 ground, and subsequent infiltration across the soil (e.g., Whipkey et al., 2000; Lorrai & Fanfani,
399 2007, and references therein). The current data may thus suggest that either marine ingressions,
400 and/or sea spray infiltration increase the pore water marine component during drier seasons, whilst
401 pore water is subjected to a sort of ‘dilution effect’, affecting sea water components (and salinity)
402 during rainy periods, due to a washout of the first soil centimetres, and transportation of the soluble
403 sea component toward deeper horizons.

404 Compositional variations are also registered in the other sampling sites, as for example, Campo
405 Pisano. In this case the element variations are more linked to precipitation/dissolution of soluble
406 salts, effects of dilution, or possibly interaction time influence. In fact, under comparatively dry
407 conditions, circulation of soil fluids is not pervasive, and the system does not approach an
408 equilibrium state; another important aspect to be considered is that Zn, an essential micronutrient, is
409 constantly taken up by plants (including *P. lentiscus* – see below). Plant physiology is therefore at
410 the same time influencing and influenced by element concentration in soil pore water.

411 An added value of field pore water chemistry monitoring is also the possibility to perform element
412 speciation in solution, offering a further ‘tile’ for the understanding of interface processes between
413 hydrosphere and biosphere. In fact, as pinpointed by other authors (e.g. Moreno-Jiménez et al.,

2011 and references therein), the soluble fraction will interact differently with plant roots as a function of element speciation; for instance Shahid et al. (2012, 2014) observed how organic ligands are capable to modify Pb speciation by forming organo-metallic complexes of different bioavailability. In this study we observe how the same concentration of some element in pore water (e.g. Zn) could be characterised by differences in speciation at different sites/times. Though beyond the purpose of this study, the understanding of how aqueous speciation may influence metal uptake by *P. lentiscus* could be an interesting subject of further investigation. The associated use of PHREEQC and WHAM programs also permitted to identify which heavy metals are preferentially present as free ions or bound to colloidal fulvic acids, and possible speciation differences from site to site.

In general, from equilibrium calculations, the soil/pore water contact time appears sufficient for reaching equilibrium conditions with several mineral phases, mostly carbonates, present in the soil (e.g. Ca-Mg carbonates, hydrozincite, cerussite, gypsum). This allows to evaluate which minerals are mostly responsible for controlling element mobility. This control is not expected to vary in a short time. However, if mineral abundance is expected to vary, e.g. because of alteration, it is possible to hypothesise a change of pore water quality in medium/long-time term. This is particularly true for 'soil' constituted by residual mining material as in Campo Pisano, more subjected to rapid alteration.

A potential limitation of this field-based approach could be that, in Mediterranean climates, during dry periods, pore water is not enough to be sampled, dictating and altering the sampling period distribution depending on climatic conditions. However, information on variations due to seasonal, climatic and morphological conditions is critical for the understanding of the physiological response of plants in the geographic context in which they occur. Laboratory-based methods fail to supply such information, and therefore long-term field studies, such as soil pore water monitoring, are required.

439 In terms of environmental risk, the concentrations of metals in pore waters can be usefully
440 compared with limits established by Italian laws (D.lgs 152/2006) for subsurface waters (Tables 4a
441 and 4b). These limits are exceeded for Pb in most samples, and in many samples at P9 also for Zn,
442 Mn, and in three samples also for Cd; Mn limits are exceeded in some samples at Campo Pisano
443 (P1 and P3). Therefore, based on present data, there is a potential impact for heavy metals in the
444 area, especially at Sa Masa. It is interesting to notice that Campo Pisano, considered one of the
445 ‘hazard centres’ of the district, does not show the highest levels of heavy metals neither in soils, nor
446 in pore waters. On the other hand, with respect to the other studied sites, the absence at Campo
447 Pisano of a vegetation cover limiting wind and water erosion makes this site a potential centre of
448 mechanical dispersion of contaminants.

449 Considering the potential mobilization to the biosphere, Concas (2014) showed that Pb is much less
450 mobile than Zn with respect to uptake by *P. lentiscus*. This limited Pb uptake was ascribed to a
451 combination of the lower Pb mobility, and of a physiological mechanism of exclusion (Zn is an
452 essential micronutrient, whereas Pb has no known physiological function, and may have phytotoxic
453 effects – Shahid et al., 2012). Concas (2014) also showed that Pb and Zn uptake of *P. lentiscus*
454 varies seasonally. Since field pore water and plant sampling did not occur at the same time (plants
455 were sampled in May and September 2012), it is not possible to compare directly plant uptake and
456 metal concentration of the pore water. Moreover, plant uptake is clearly influenced also by the total
457 amount of available pore water, and not only by metal concentrations. This aspect could well be
458 worthy a future step of investigation. The authors notice here that this kind of information could be
459 useful for the management of a mining waste dump subjected to phytostabilization. For example, a
460 water-saving watering system could be planned in specific periods of the year in order to modify
461 pore water composition, to obtain a decrease of some element when necessary. As a consequence of
462 Zn mobilization to the biosphere, there is a potential risk that this metal could enter the trophic
463 chain. On the other hand, phytostabilization actions using *P. lentiscus* as a pioneer species should

not be impaired, inasmuch as this species is well tolerant to Zn (Bacchetta et al., 2012; Concas, 2014).

5. Conclusions

Field sampling and chemical monitoring of soil pore water in the major abandoned mining district of Iglesiente (SW Sardinia) confirmed that pore water is a rapid and easy method to collect reliable information on the potential risk of a contaminated soil.

Soil pore waters chemistry in the studied sites reflects the mineralogy of the local soil, and suggests an approach to equilibrium with coexisting solid phases. This aspect permits to easily evaluate which minerals are likely responsible for controlling (toxic) element mobility.

With respect to laboratory tests on metal mobility, the analysis of pore water permits to evaluate trace elements mobility, and the consequent environmental risk, also following pore water seasonal changes both in qualitative and quantitative terms. Pore water represents the most available fraction of the overall soil matrix for plant uptake, therefore allowing a direct comparison with possible seasonal changes in metal uptake by plants. In fact, in a companion study of the local species *P. lentiscus*, local and seasonal variations of metal (Zn, Pb and Hg) concentrations in different parts of the plant were detected. Such variations may be partially a response to local/seasonal changes of pore water quantitative/qualitative characteristics. This kind of information could be useful for the management of a mining waste dump interested by phytostabilization.

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660

661	Table captions
662	
663	Table 1. Selected soil properties at the sampling sites
664	
665	Table 2a and 2b. Major and selected trace element analysis of soils at the sampling sites,
666	distinguished for horizons
667	
668	Table 3a and 3b. Pore water parameters (T°, pH, conductivity) and major chemistry distinguished
669	for sampling site, sampling time, and sampling method.
670	
671	Table 4a and 4b. Selected trace elements in pore waters distinguished for sampling site, sampling
672	time, and sampling method. Bold font indicates values above limits established by Italian laws
673	(D.lgs 152/2006) for subsurface waters.
674	
675	Table 5. Main element speciation in pore waters as determined by PHREEQC and WHAM codes.

676 **Figure captions**

677
678 Figure 1. Schematic map of the study area, with location of sampling points.

679
680 Fig. 2. a) general view of the Campo Pisano experimental plots established in 2008 by Bacchetta et
681 al. (2012), pointing those selected for this study; b) and c) vertical sections of ‘soils’ in Plot 1 and
682 Plot 3; in the first (untreated material) *P. lentiscus* planted in 2008 did not survive, whereas several
683 individuals survived in Plot 3, where compost was added as amendment.

684
685 Fig. 3. Piper diagram illustrating the variability in major ion composition of the studied pore waters.

686
687 Fig. 4. Saturation indexes for selected minerals, distinct for sampling site (symbol), and ordered for
688 sampling time (from right to left). The solid line (SI = 0) indicates equilibrium between mineral and
689 solution. See text for the assessment of the role of selected minerals from (a) to (h) in controlling
690 element mobility in pore waters.

691
692 Fig. 5. Na vs Cl plot of pore water samples from Sa Masa site (P9). The linear trend suggests a co-
693 variation of the two elements due to seasonal variations.

Table 1

Soil	Horizon	Depth cm	Texture			Textural class ^a	pH (H ₂ O)	OC g kg ⁻¹
			Sand	Silt %	Clay			
P1	^ACm	0–0.3/0.5	77.7	20.9	1.4	ls	7.6	11
	^AC1	0.3/0.5–8/14	82.5	16.7	0.8	ls	7.5	9
	^AC2	8/14–16.5/20.5	69.6	29.3	1.1	sl	7.3	14
	2^C	16.5/20.5–>30	68.4	28.3	3.3	sl	4.5	2
P3	^Ap1	0–1.5/1.8	73.8	24.8	1.4	ls	7.2	61
	^Ap2	1.5/1.8–15/17	77.9	21.3	0.8	ls	7.1	66
	2^C	15/17–>22	66.8	31.1	2.1	sl	4.8	5
P5	A	0–15	44.1	41.6	14.3	l	7.3	43
	AB	15–28	30.7	39.9	29.4	cl	7.3	27
	Bw	28–60/65	13.6	26.6	59.8	c	7.3	11
	R	>60/65						
P6	A	0–10	44.1	43.8	12.1	l	7.1	37
	Bw	10–37/50	31.5	41.2	27.3	cl	7.5	18
	R	>37/50						
P9	A	0–8	47.2	49.8	3.0	l	7.5	25
	2C1	8–12	18.4	76.2	5.4	sil	7.8	9
	3C2	12–25	73.6	24.6	1.8	ls	7.8	6
	4C3	25–40	53.0	45.9	1.1	sl	7.8	5
	5C4	40–59	34.1	63.6	2.3	sil	8.0	6
	6C5	59–>120	86.9	12.1	1.0	ls	8.1	5

^a ls = loamy sand; sl = sandy loam; l = loam; cl = clay loam; c = clay; sil = silt loam.

Soil	Horizon	Depth (cm)	LOI	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	Other*	Tot
		(cm)	%	%	%	%	%	%	%	%	%	%	%	%	%
P1	^ACm	0-0.3/0.5	28.84	0.40	13.9	3.81	14.3	0.04	0.59	23.2	0.13	0.24	13.5	1.52	100
	^AC1	0.3/0.5-8/14	26.69	0.33	13.5	4.13	14.5	0.04	0.60	25.0	0.12	0.25	10.7	1.47	97.0
	^AC2	8/14-16.5/20.5	24.25	0.61	15.2	2.84	11.9	0.04	0.53	26.0	0.13	0.23	17.0	1.69	100
	2^C	16.5/20.5->30	13.70	0.25	0.50	2.57	9.21	0.03	0.49	23.9	0.12	0.02	48.5	0.79	100
P3	^Ap1	0-1.5/1.8	25.32	0.41	5.43	5.71	21.9	0.89	0.93	20.6	0.16	0.20	17.6	1.12	100
	^Ap2	1.5/1.8-15/17	24.71	0.52	9.46	4.28	18.9	0.25	0.82	23.2	0.16	0.17	16.8	1.00	100
	^2C	15/17- >22	12.75	0.11	0.18	2.25	7.67	0.05	0.40	25.8	0.09	0.02	50.2	0.65	100
P5	A	0-15	12.56	0.23	1.19	20.8	52.1	0.15	1.92	0.62	0.44	0.49	8.15	1.55	100
	Ab	15-28	10.65	0.25	1.41	21.3	50.9	0.13	2.27	0.47	0.53	0.51	9.79	1.94	100
	Bw	28-60/65	10.50	0.22	1.32	26.9	44.7	0.08	2.59	0.34	0.45	0.40	11.7	0.90	100
P6	A	0-10	11.43	0.60	1.96	16.9	54.0	0.15	2.84	0.95	0.81	0.96	8.91	0.61	100
	Bw	10-37/50	8.51	0.49	1.80	21.2	52.8	0.12	2.79	0.60	0.76	0.87	9.38	0.68	100
P9	2C1	8-12	28.89	0.65	5.33	3.28	23.1	0.04	0.39	32.4	0.17	0.18	3.68	2.69	100
	3C2	12-25	31.68	0.48	6.61	2.48	18.2	0.03	0.25	35.7	0.17	0.22	2.71	2.23	100
	4C3	25-40	33.48	0.41	6.61	1.17	14.4	0.02	0.19	40.1	0.09	0.22	2.23	1.73	100
	5C4	40-59	35.37	0.46	7.99	1.30	10.5	0.02	0.19	38.7	0.09	0.24	3.89	1.96	100
	6C5	59- >120	31.77	0.62	8.22	1.31	10.3	0.02	0.21	35.2	0.09	0.20	9.24	4.13	100

° Except the A horizon at the P9 location – see text

*Sum of elements in Table 2b

Table 2a

Profile	Horizon	Depth (cm)	Cd	Cu	Ni	Pb	Zn
					mg/kg		
P1	^ACm	0-0.3/0.5	70	52	< 16	2180	12932
	^AC1	0.3/0.5-8/14	72	44	< 16	2180	12402
	^AC2	8/14-16.5/20.5	78	92	< 16	2126	14646
	2^C	16.5/20.5- >30	15	56	< 16	2698	5119
P3	^Ap1	0-1.5/1.8	54	54	< 16	1760	9360
	^Ap2	1.5/1.8-15/17	54	51	< 16	1566	8327
	^2C	15/17- >22	16	57	< 16	2776	3666
P5	A	0-15	6	56	39	13642	1779
	Ab	15-28	<4	54	39	17697	1655
	Bw	28-60/65	<4	56	53	7134	1822
	R	60/65- >60/65	10	10	< 16	1754	426
P6	A	0-10	30	37	41	1360	4680
	Bw	10-37/50	30	31	44	1453	5244
	R	37/50- >37/50	<4	<8	< 16	<d.l.	1097
P9	A	0-8	265	330	< 16	37616	220946
	2C1	8-12	153	72	< 16	4300	22400
	3C2	12-25	89	49	< 16	3401	18805
	4C3	25-40	70	45	< 16	3398	13792
	5C4	40-59	92	45	< 16	2335	17122
	6C5	59- >120	146	83	< 16	5927	35173

Table 2b

Table
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Site	sample	t (°C)				pH				λ (μS cm ⁻¹)				alkalinity (mg L ⁻¹)				Organic Carbon (mg L ⁻¹)			
		Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr
P1	1	14.5	11.2	14.5	-	9.21	8.26	7.15	-	-	1818	2060	-	18	-	57	-	11.4	<0.04	3.3	-
P3	2	17.2	10.9	15.5	-	8.73	8.51	7.38	-	-	1240	2020	-	44	89	147	-	12.6	7.1	10.7	-
long lysimeter	4a	13.9	11.2	13	-	8.12	7.39	7.31	-	-	2630	2770	-	69	180	307	-	6.48	1.9	1.8	-
	4b	13.7	11.3	12.2	-	7.91	7.41	7.11	-	-	3750	2840	-	47	158	314	-	6.93	2.3	2.1	-
	4c	13.7	10.8	11.3	-	7.72	7.03	7.26	-	-	3240	2740	-	111	167	307	-	3.25	1.6	1.6	-
short lysimeter	5a	13.7	10.7	12.6	-	8.31	7.88	7.55	-	-	2900	2450	-	55	114	237	-	8.1	<0.04	2.9	-
	5b	-	10.6	12.3	-	-	7.64	7.39	-	-	2600	2420	-	-	136	245	-	-	1.2	4.8	-
P9 rizhometer	19	-	-	-	24	-	-	-	7.93	-	-	-	2440	-	-	-	151	-	-	-	5.1
P9 rizhometer	22	-	-	-	16.8	-	-	-	7.78	-	-	-	2180	-	-	-	152	-	-	-	5.62
P9 rizhometer	25	-	-	-	20	-	-	-	7.62	-	-	-	2460	-	-	-	154	-	-	-	3.97
short lysimeter	25	-	-	-	18.7	-	-	-	7.5	-	-	-	2620	-	-	-	192	-	-	-	4.79
P5	6a	-	-	15.2	-	-	-	8.87	-	-	-	566	-	-	-	243	-	-	-	3.3	-
	6b	-	11.8*	14.3	-	-	9.14*	8.87	-	-	577*	706	-	-	178*	275	-	-	4.3*	4.1	-
	6c	-	11.8*	15.9	-	-	9.14*	8.8	-	-	577*	696	-	-	178*	252	-	-	4.3*	3.8	-
P6	7a	-	-	14.2	-	-	-	8.9	-	-	-	797	-	-	-	278	-	-	-	4.0	-
	7b	-	11.4	14.8	-	-	9.16	9.02	-	-	910	961	-	-	210	339	-	-	<0.04	4.7	-
	7c	-	-	12.5	-	-	-	9.05	-	-	-	679	-	-	-	401	-	-	-	2.4	-

* = 6b + 6c average; - = not analysed

Table 3a

Site	sample	Cl (mg L ⁻¹)				SO ⁴ (mg L ⁻¹)				Ca ²⁺ (mg L ⁻¹)				Mg ²⁺ (mg L ⁻¹)				Na ⁺ (mg L ⁻¹)				K ⁺ (mg L ⁻¹)			
		Dec	Jan	Feb	Apr	Dec	Jan	Feb	Apr	Dec	Jan	Feb	Apr	Dec	Jan	Feb	Apr	Dec	Jan	Feb	Apr	Dec	Jan	Feb	Apr
P1	1	30	16	24	-	855	1480	1290	-	316	460	469	-	34	98	54	-	18	11	14	-	1	1	0.0	-
P3	2	14	43	10	-	783	1044	1082	-	314	393	468	-	39	62	45	-	7	22	9	-	2	6	0.9	-
P9 long lysimeter	4a	443	368	272	-	1385	1186	962	-	433	322	279	-	156	132	105	-	326	268	205	-	26	21	17	-
	4b	448	437	279	-	1429	1404	1070	-	438	376	294	-	161	157	106	-	332	310	205	-	27	24	18	-
	4c	439	357	270	-	1382	1184	978	-	422	332	275	-	148	122	100	-	319	262	198	-	24	21	18	-
P9 short lysimeter	5a	398	337	255	-	1252	1187	920	-	338	295	259	-	135	133	103	-	285	255	194	-	21	21	16	-
	5b	-	346	258	-	-	1186	924	-	-	326	271	-	-	119	98	-	-	253	197	-	-	21	17	-
P9 rizhometer	19	-	-	-	274	-	-	-	757	-	-	-	219	-	-	-	75	-	-	-	168	-	-	-	16
P9 rizhometer	22	-	-	-	260	-	-	-	893	-	-	-	262	-	-	-	83	-	-	-	184	-	-	-	16
P9 rizhometer	25	-	-	-	302	-	-	-	753	-	-	-	286	-	-	-	78	-	-	-	178	-	-	-	17
P9 short lysimeter	25	-	-	-	256	-	-	-	919	-	-	-	259	-	-	-	91	-	-	-	187	-	-	-	17
P5	6a	-	-	23		-	-	7		-	-	36		-	-	36	-	-	-	26	-	-	-	10	-
	6b	-	31*	30		-	6*	4		-	23*	23		-	41*	67	-	-	23*	34	-	-	9*	11	-
	6c	-	31*	18		-	6*	15		-	23*	42		-	41*	55	-	-	23*	26	-	-	9*	9.9	-
P6	7a	-	-	64		-	-	14		-	-	36		-	-	66	-	-	-	33	-	-	-	6.2	-
	7b	-	168	123		-	14	16		-	27	31		-	120	69	-	-	68	62	-	-	28	25	-
	7c	-	-	40		-	-	13		-	-	0		-	-	54	-	-	-	43	-	-	-	6.7	-

*= 6 b + 6c average; - = not analysed

Table 3b

Site	sample	Zn µg L ⁻¹				Pb µg L ⁻¹				Cd µg L ⁻¹			
		Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr
P1	1	20	126	172	-	22	17	18	-	-	<0.4	2.3	-
P3	2	38	145	206	-	36	18	32	-	-	<0.4	3.6	-
P9 long lysimeter	4a	127	6226	4324	-	21	30	<5	-	-	<0.4	1.4	-
	4b	117	6261	4613	-	12	28	<5	-	-	<0.4	2.3	-
	4c	481	7861	5666	-	20	23	14	-	-	<0.4	3.7	-
P9 short lysimeter	5a	60	1497	1516	-	16	23	18	-	-	<0.4	2.5	-
	5b	-	2530	3195	-	-	19	23	-	-	<0.4	7.1	-
P9 rizhometer	19	-	-	-	1665	-	-	-	64	-	-	-	5
P9 rizhometer	22	-	-	-	2056	-	-	-	10	-	-	-	7
P9 rizhometer	25	-	-	-	2274	-	-	-	18	-	-	-	10
P9 short lysimeter	25	-	-	-	1597	-	-	-	<5	-	-	-	3
P5	6a	-	-	35	-	-	-	<5	-	-	-	<1.3	-
	6b	-	31*	41	-	-	64*	18.6	-	-	<0.4*	<1.3	-
	6c	-	31*	127	-	-	64*	<5	-	-	<0.4*	<1.3	-
P6	7a	-	-	23	-	-	-	<5	-	-	-	<1.3	-
	7b	-	24	30	-	-	46	<5	-	-	<0.4	<1.3	-
	7c	-	-	18	-	-	-	13	-	-	-	<1.3	-

*= b + c average; - = not analysed

Table 4a

Site	sample	Mn µg L ⁻¹				Fe µg L ⁻¹				Cu µg L ⁻¹			
		Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr	Dec	Jan	Febr	Apr
P1	1	9	10	<0.01	117	0.4	13	119	-	8.0	<0.5	<1.2	-
P3	2	16	13	<0.01	200	98	19	<5.3	-	26	4.8	2	-
P9 long lysimeter	4a	140	226	141	74	47	11	7	-	4.9	5.9	11	-
	4b	68	230	62	73	<0.1	13	<5.3	-	4.6	1.9	3	-
	4c	63	92	5	70	<0.1	6.0	<5.3	-	2.2	1.7	2	-
P9 short lysimeter	5a	15	59	3	77	15	2.2	<5.3	-	6.0	4.6	8.9	-
	5b	-	22	<0.01	-	-	15	<5.3	-	-	0.7	4	-
P9 rizhometer	19	-	-	-	<0.01	-	-	-	-	-	-	-	<1.2
P9 rizhometer	22	-	-	-	<0.01	-	-	-	-	-	-	-	<1.2
P9 rizhometer	25	-	-	-	<0.01	-	-	-	-	-	-	-	4
P9 short lysimeter	25	-	-	-	<0.01	-	-	-	-	-	-	-	2
P5	6a	-	-	-	-	-	-	-	-	-	-	-	-
	6b	-	9*	-	-	-	23*	<5.3	-	-	7*	4.3	-
	6c	-	9*	-	-	-	23*	<5.3	-	-	7*	<1.2	-
P6	7a	-	-	-	-	-	-	<5.3	-	-	-	<1.2	-
	7b	-	9	-	-	-	24	<5.3	-	-	8	<1.2	-
	7c	-	-	-	-	-	-	<5.3	-	-	-	<1.2	-

*= b + c average; - = not analysed

Table 4b

Table
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Site	sampler	Species* (PHREEQC)	fraction bound to colloidal FA (WHAM)
P1	1 - Dec	Ca ²⁺ , CaSO ₄ , CuOH ⁺ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbOH ⁺ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (80%), Zn (3.5%), Pb (0.2%)
	1 - Jan	Ca ²⁺ , CaSO ₄ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbOH ⁺ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	no O.C.
	1 - Febr	Ca ²⁺ , CaSO ₄ , Mg ²⁺ , MgSO ₄ , Pb ²⁺ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Zn (2.4%), Cd (1.15%), Pb (0.015%)
P3	2 - Dec	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (60%), Zn (5%), Pb (0.1%)
	2 - Jan	Ca ²⁺ , CaSO ₄ , CuOH ⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , MnCO ₃ , PbCO ₃ , PbOH ⁺ , Zn ²⁺ , ZnSO ₄	Cu (55%), Zn (3.2%), Pb (0.06%)
	2 - Febr	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (99%), Zn (8.8%), Cd (3.6%), Pb (70%)
P5	6b+c - Jan	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Cu(CO ₃) ₂ ²⁻ , Mg ²⁺ , MgSO ₄ , MnCO ₃ , Mn ²⁺ , PbCO ₃ , Pb(CO ₃) ₂ ²⁻ , PbOH ⁺ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	Cu (39%), Zn (3.5%)
	6a - Febr	Ca ²⁺ , CaCO ₃ , Mg ²⁺ , MgCO ₃ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	Zn (4.8%)
	6b - Febr	Ca ²⁺ , CaCO ₃ , CuCO ₃ , Cu(CO ₃) ₂ ²⁻ , Mg ²⁺ , MgCO ₃ , PbCO ₃ , Pb(CO ₃) ₂ ²⁻ , Zn ²⁺ , ZnCO ₃	Cu (60%), Zn (3%), Pb (0.9%)
	6c - Febr	Ca ²⁺ , CaCO ₃ , Mg ²⁺ , MgCO ₃ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	Zn (3%)
P6	7b - Jan	Ca ²⁺ , CuCO ₃ , Cu(CO ₃) ₂ ²⁻ , Mg ²⁺ , MgCO ₃ , MnCO ₃ , Mn ²⁺ , PbCO ₃ , Pb(CO ₃) ₂ ²⁻ , PbOH ⁺ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	no O.C.
	7a Febr	Ca ²⁺ , CaCO ₃ , Mg ²⁺ , MgCO ₃ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	Zn (5%)
	7b - Febr	Ca ²⁺ , CaCO ₃ , Mg ²⁺ , MgCO ₃ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	Zn (5.5%)
	7c - Febr	Ca ²⁺ , CaCO ₃ , Mg ²⁺ , MgCO ₃ , PbCO ₃ , Pb(CO ₃) ₂ ²⁻ , Zn(OH) ₂ , Zn ²⁺ , ZnCO ₃	Zn (5%), Pb (1%)
P9 long lysimeter	4a - Dec	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (20%), Zn (1%)
	4a - Jan	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Cu ²⁺ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (4.4%), Zn (0.05%)
	4a - Febr	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (8.1%), Zn (0.4%), Cd (0.3%)

	4b - Dec	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (12%), Zn (0.4%), Cd (0.3%)
	4b - Jan	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Cu ²⁺ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (5.8%), Zn (0.06%)
	4b - Febr	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , Zn ²⁺ , ZnSO ₄	Cu (12%), Zn (0.4%), Cd (0.3%)
	4c - Dec	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (13%), Zn (0.6%)
	4c - Jan	Ca ²⁺ , CaSO ₄ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (2.7%), Zn (0.2%)
	4c - Febr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (9.7%), Zn (0.4%), Cd (0.2%), Pb (1.2%)
p9	5a+5b - Dec	Ca ²⁺ , CaSO ₄ , CuOH ⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (66%), Zn (4%), Pb (0.05%)
	5a - Jan	Ca ²⁺ , CaSO ₄ , CuCO ₃ , CuOH ⁺ , Cu ²⁺ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	no O.C.
	5a - Febr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (22%) Zn (1%), Cd (0.7%), Pb (2%)
	5b - Jan	Ca ²⁺ , CaSO ₄ , CuCO ₃ , CuOH ⁺ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Cu (0.06%), Zn (0.3%)
	5b - Febr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , PbCO ₃ , Zn ²⁺ , ZnSO ₄	Cu (22%), Zn (1%), Cd (0.7%), Pb (2%)
	ryzhom 19 Apr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , Mg ²⁺ , MgSO ₄ , PbCO ₃ , PbOH ⁺ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Zn (2.8%), Cd (1.3%), Pb (5.6%)
	ryzhom 22 Apr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , PbOH ⁺ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Zn (2.3%), Cd (1.3%), Pb (4%)
	ryzhom 25 Apr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , PbCO ₃ , PbOH ⁺ , Pb ²⁺ , Zn ²⁺ , ZnSO ₄	Zn (2.3%), Cd (0.6%), Pb (37%)
	lysim 25 Apr	Ca ²⁺ , CaSO ₄ , CdCl ⁺ , Cd ²⁺ , CuCO ₃ , Mg ²⁺ , MgSO ₄ , Mn ²⁺ , MnSO ₄ , Zn ²⁺ , ZnSO ₄	Cu (94%), Zn (3%), Cd (0.9%)

*listed for each element in order of relative abundance; only species present in amounts >5% are reported

Table 5.

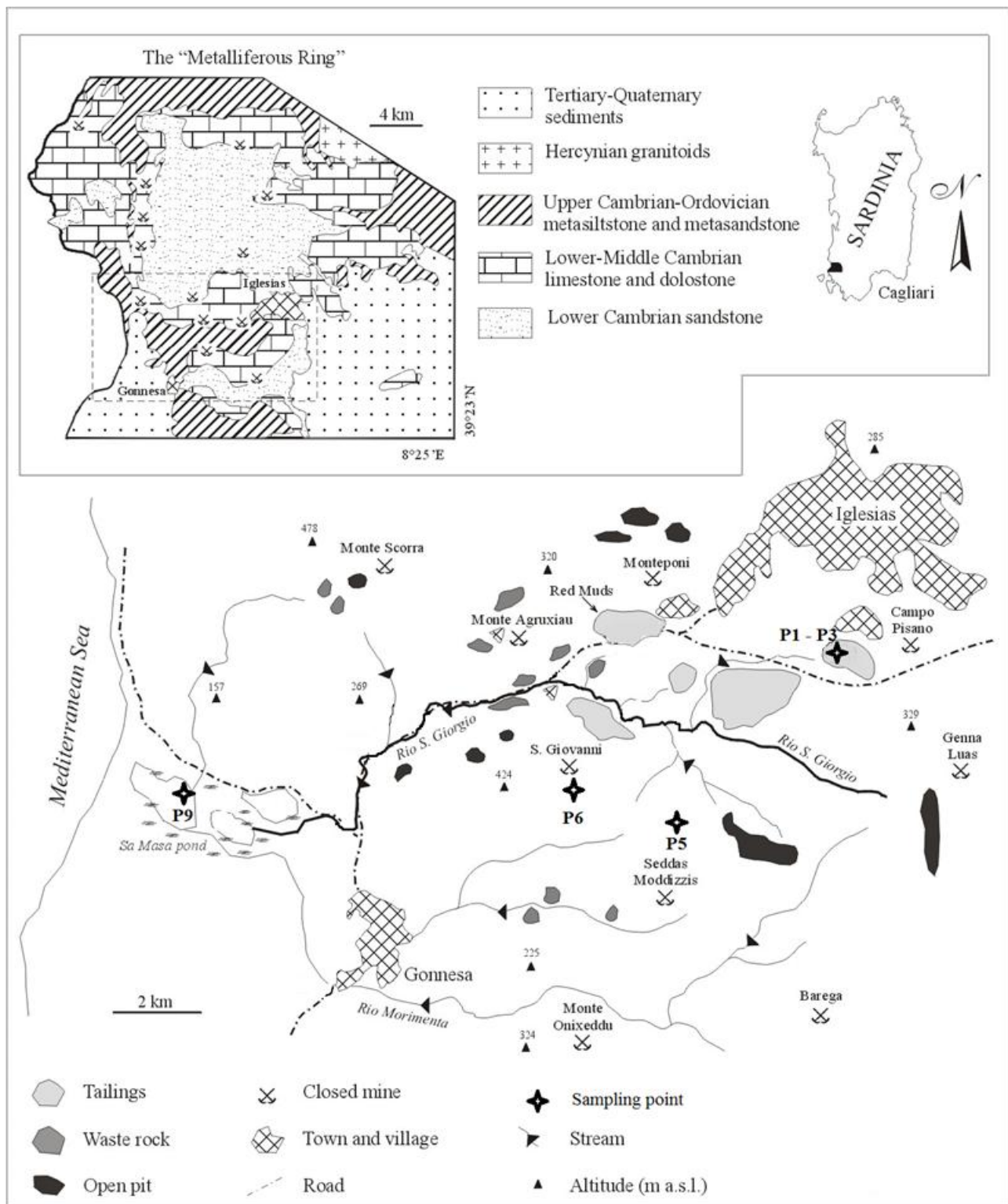


Fig. 1

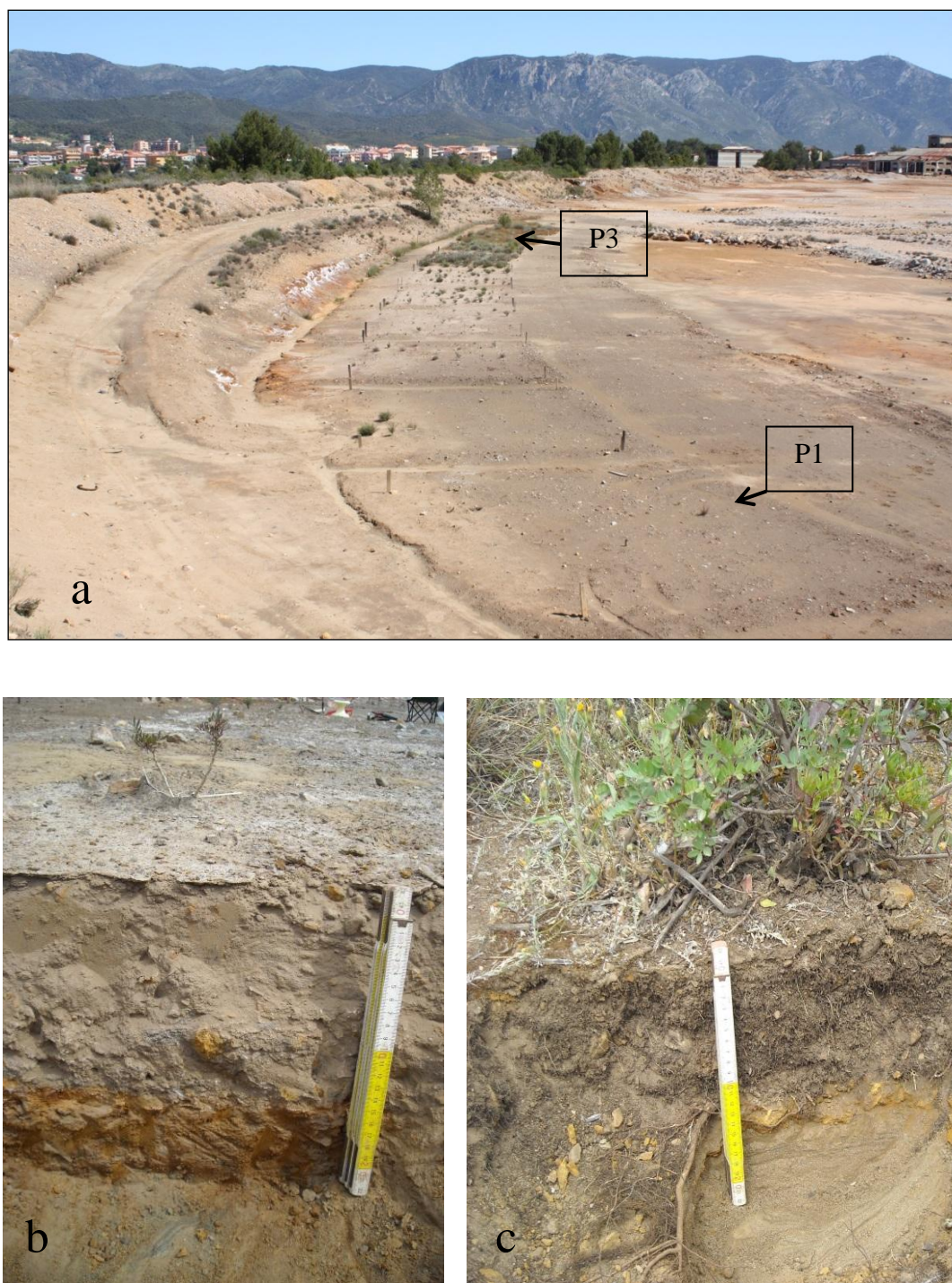


Fig 2

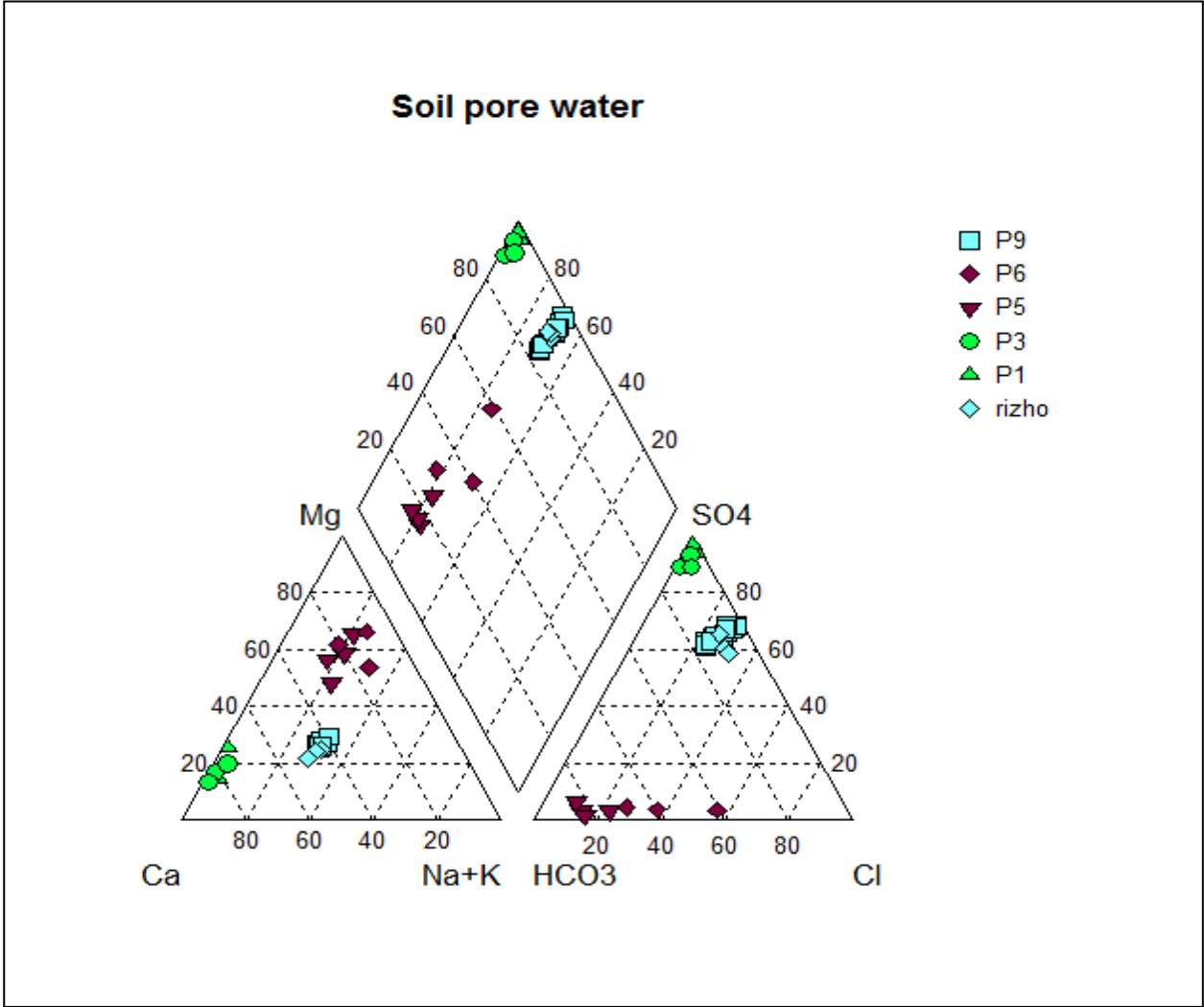


Fig. 3

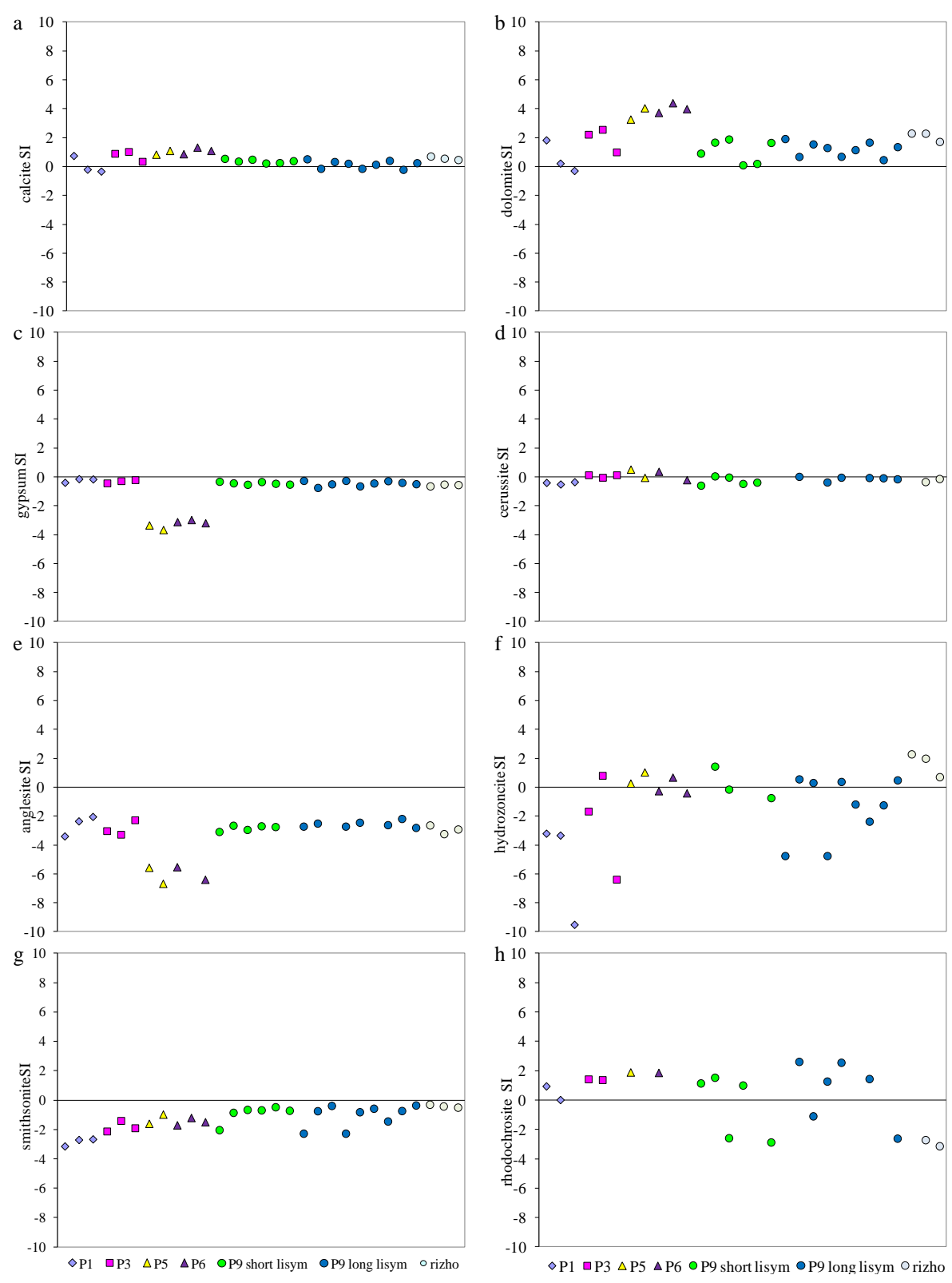


Fig. 4

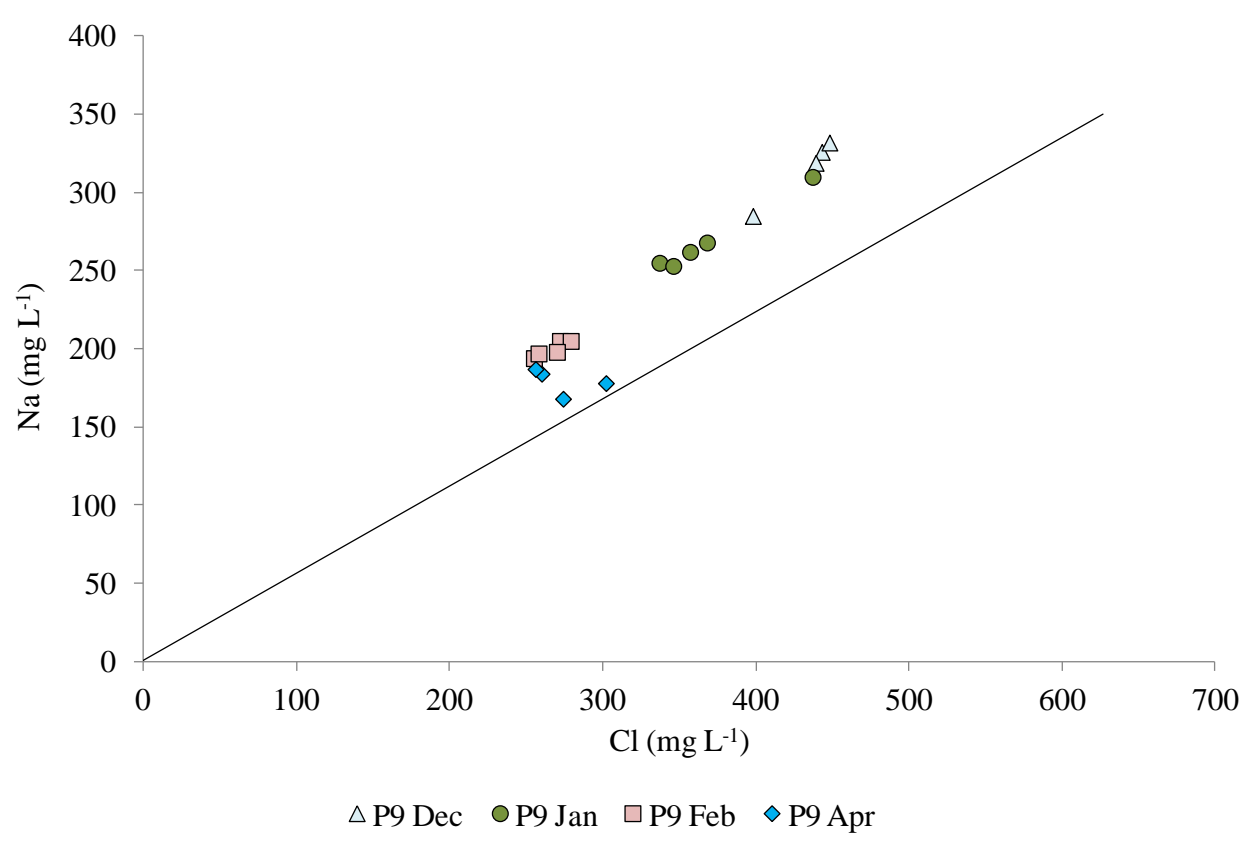


Fig. 5